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Towards Internal Structuring of Electrospun Fibers by Hierarchical Self-Assembly of Polymeric Comb-Shaped Supramolecules**

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Control of nanometer-scale structures and self-assembly combining different length scales has recently been heavily pursued in the quest for rational tailoring of material properties and functionalities in a "bottom–up" fashion.[1–8] It has remained a challenge, as it may require simultaneous application of several mechanisms and techniques. The present work combines structures at the nanometer and tens-of-nanometers length scales by hierarchical self-assembly of polymeric comb-shaped supramolecules within fibrous structures whose dimensions are an order of magnitude larger. Electrostatic spinning, also known as electrospinning,[9–11] has here been used to prepare fibers of polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) with diameters 200–400 nm, in which a nominal stoichiometric amount of 3-*n*-pentadecylphenol (PDP) is hydrogen-bonded to the latter block to form the supramolecular complex PS-*b*-P4VP(PDP)$_{1.0}$. Self-assembly between PS and P4VP(PDP)$_{1.0}$ leads to order on the length scale of ca. 30 nm, whereas self-assembly on the length scale of 3.9 nm takes place within the P4VP(PDP)$_{1.0}$ domains, as suggested by the corresponding bulk matter.[12,13] Interestingly, the hydrogen bonding tolerates the harsh electrospinning conditions, as shown by small-angle X-ray scattering (SAXS) and NMR measurements. After electrospinning, the hydrogen-bonded PDP molecules can be cleaved, leaving fibers with internal nanometer-scale porosity that could open new possibilities, e.g., for controlled release and absorption.

Self-assembly leads to nanostructured materials and hierarchy based on competition between attractive and repulsive interactions.[2,4] Repulsive chemical groups can be bonded using sufficiently strong physical interactions (these have been extensively studied in the context of supramolecular chemistry[14]) that allow reversible purging of the attractive interactions in order to tune the structures and functions.[4,15–17] Surfactants and amphiphiles are known to self-assemble on the scale of a few nanometers,[18] whereas in block copolymers,[5] the structures that form are typically an order of magnitude larger. Alternatives to produce well-defined self-assembling structural units at the larger length scale of a few hundred nanometers seem to be scarce. Spherical colloidal particles have been extensively used,[19] and have even been combined with block copolymers.[20] In addition, hydrodynamic instabilities have been used to prepare honeycomb structures.[21,22] Lithography also becomes feasible at this length scale.[23,24] A particularly straightforward technique to prepare fibers with diameters at this length scale—i.e., fibers that are drastically thinner than those produced using conventional fiber preparation methods, such as melt, dry, and wet spinning—is electrospinning.[10] Electrospinning involves application of an electric field between a capillary tip and a collector by a high-voltage source. A pendant droplet of polymer solution at the capillary tip is transformed to a hemispherical shape and then into a conical shape, also known as Taylor cone, by the electric field. When the effect of the electric field becomes stronger than the surface tension of the polymer solution, the solution is ejected towards the metallic collector. If the concentration (and hence, viscosity) of the solution is not suitable (i.e., no entanglement of the polymer chains take place), the jet breaks up into droplets. However, if the viscosity is high enough, indicating that the polymer chains are entangled, a continuous jet is formed. The field accelerates the jet and it becomes unstable. Whipping instability is one of the possible instabilities that may occur in an electrified fluid jet.[25] The rapidly whipping jet undergoes high stretching during its complicated path through the electric field. The initially single jet can also divide into multiple filaments by radial-charge repulsion, a process known as "splaying", which can be responsible for the formation of fibers with diameters on the meso- and nanometer scales. The solvent evaporates during the spinning process, and dry, thin fibers can be obtained on the collector plate using appropriate process parameters. In some fibers there is a significant amount of residual solvent and either merged or slightly merged fibers can be obtained upon reaching the collector.

The science behind electrospinning has previously been studied in some detail and the processing parameters have been described.[11,25,26] However, few studies have been published on the internal structure formation within the fibers using self-assembled polymer systems or block copolymers,[27,28] which are known to form a wide variety of nanometer-scale structures in bulk or in films, and to allow various functionalities.

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In this paper, we investigate supramolecular hierarchical structures whose formation combines electrospinning and a self-assembling block copolymer/amphiphile model system, PS-*b*-P4VP(PDP)$_{1.0}$. Previous studies in bulk have shown the existence of self-assembly between PS and P4VP(PDP)$_{1.0}$, and a second level of self-assembly within the P4VP(PDP)$_{1.0}$ domains between the non-polar alkyl tails of PDP and the polar P4VP chains.[4,13,16] The studies in bulk showed that, by selecting relatively long PS blocks, lamellar-*within*-spherical structures are achieved;[13] Figure 1 shows the intended structures within the electrospun fibers that we pursued in this work. Highly developed ordering of block copolymers can be achieved in bulk or in

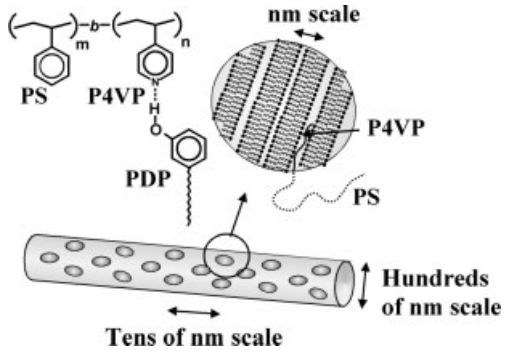

Figure 1. Schematic picture of the electrospun fibers that were the aim of this work. The preparation requires control of three characteristic length scales. The largest length scale is controlled by the electrospinning process, whereas the two smaller length scales are controlled by the lamellar-*within*-spherical self-assembly of PS-*b*-P4VP(PDP)$_{1.0}$.

films, but this usually requires particularly slow evaporation of the solvent and careful annealing.[5] Hence, we expected the formation of the self-assembled structure by electrospinning to be non-trivial for two reasons. First, under the electrospinning process, solvent evaporation is extremely rapid. In this work, it turns out that self-assembled structures can be achieved although the order is relatively poor. Second, the hydrogen-bonded supramolecular structures survive the rough processing conditions in spite of their relative weakness. Finally, we show that mesoporous structures can be achieved upon cleaving PDP even in the case of electrospun fibers, which is qualitatively similar to what has previously been observed in bulk.[16]

Structure formation at the three different length scales was studied using various methods. The external structures of the electrospun fibers were examined using atomic force microscopy (AFM). The diameters were observed to be typically ca. 200–400 nm (Fig. 2) and are relatively well controlled by tuning the process parameters.

The internal structure of the fibers was studied using transmission electron microscopy (TEM). The fibers shown in Figure 3c and Figures 4b,c were produced on a rotating collector, and that shown in Figure 3b was produced from a fibrous web spun on a static collector. Microtomed sections were stained with iodine, which is known to selectively attach to the pyri-

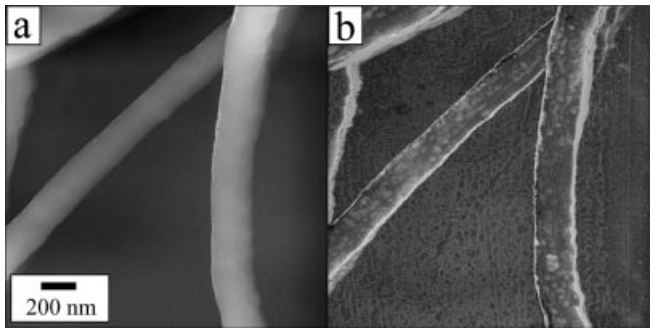

Figure 2. AFM images of electrospun fibers of PS-*b*-P4VP(PDP)$_{1.0}$. Molecular weights are 238 100 g mol^{-1} and 49 500 g mol^{-1} for the PS and P4VP blocks, respectively. a) TappingMode topographical image of fibers with typical outer diameters of 200 to 400 nm. b) Phase image showing softer P4VP(PDP)$_{1.0}$ phases on the surface of the fibers.

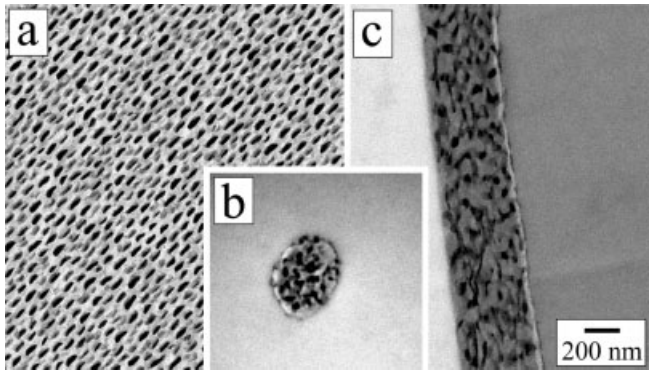

Figure 3. TEM images of PS-*b*-P4VP(PDP)$_{1.0}$ showing the structure formation at the length scale of tens of nanometers, i.e., at the block copolymer length scale. Molecular weights are 238 100 g mol^{-1} and 49 500 g mol^{-1} for the PS and P4VP blocks, respectively. a) Elongated spheres of P4VP(PDP)$_{1.0}$ in the PS matrix in the bulk phase after casting from a concentrated dimethylformamide (DMF) solution and annealing. b) The cross-sectional structure of the electrospun fiber. c) Image of the structure along the electrospun fiber. All micrographs are at the same magnification.

dine groups of the P4VP domains, and thus the P4VP domains appear darker than the PS domains.[4,12,13] The morphologies of the fibers were compared to their corresponding bulk morphologies (Figs. 3a,4a), which were spherical with elongated distortions as a result of compression during microtoming. The bulk samples were prepared using similar high-concentration solutions to those required for the electrospinning process.

Figures 3b,c show the structure of the electrospun sample. Domains are indeed observed, but they are relatively ill-shaped and not spherical. This does not come as a surprise, as the fiber formation may not be in equilibrium due to the fast evaporation and deformation that occur during electrospinning. An effort was made to thermally anneal the fibers after casting them in epoxy, but appropriate annealing conditions to improve or alter the morphology were not found. Figures 4b,c show slightly improved structures with another

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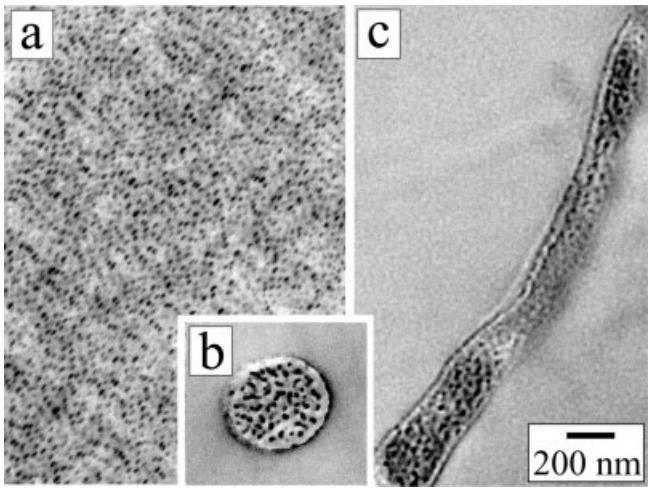

Figure 4. TEM images of PS-*b*-P4VP(PDP)$_{1.0}$ complexes. Molecular weights are 30 100 g mol^{-1} and 19 600 g mol^{-1} for the PS and P4VP blocks, respectively. a) The bulk phase after casting from a concentrated DMF solution and annealing. Dark P4VP(PDP)$_{1.0}$ spheres are located in the gray PS matrix. b) The cross-sectional structure of an electrospun fiber. c) Image of the structure along an electrospun fiber. All micrographs are at the same magnification.

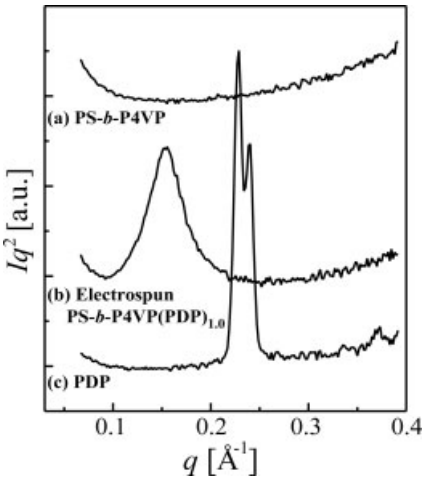

Figure 5. SAXS curves: a) PS-*b*-P4VP shows no distinct peaks in this region. b) Electrospun fiber of PS-*b*-P4VP(PDP)$_{1.0}$ shows a reflection at $q = 0.16$ Å^{-1} due to lamellar structures between the alkyl tails of PDP and the polar P4VP/phenol moieties. Molecular weights are 238 100 g mol^{-1} and 49 500 g mol^{-1} for the PS and P4VP blocks, respectively. c) PDP is crystalline and shows several reflections in the SAXS and wide-angle X-ray scattering intensity curves ($q = 0.23$ Å^{-1} and $q = 0.24$ Å^{-1} in this range).

block copolymer, which indicates that the actual morphology may be a delicate balance between polymer composition and processing conditions. More detailed research will be published later.[29] We took these results to be an indication that it is possible to achieve internal structuring of electrospun fibers using block copolymer-like self-assembly. We also point out that, in order to obtain more information on the internal structure, tomographical methods of TEM could be useful.[29]

The smallest length scale was studied using ^{1}H NMR and SAXS. A peak corresponding to the methyl group on the alkyl tail of PDP at $\delta = 0.89$ (t, 3H, CH_3, PDP), and another distinct peak corresponding to the alkyl tail of PDP at $\delta = 2.56$ (t, Ar–CH_2–R, PDP) observed in the ^{1}H NMR spectrum of electrospun PS-*b*-P4VP(PDP)$_{1.0}$ indicate that the hydrogen-bonded PDP amphiphiles were still present after electrospinning. The integrated area of the methyl peak was compared to those of the aromatic hydrogens ($\delta = 6.3$–7.2 (m, Ar–H, PS-*b*-P4VP and PDP)) in the complex, which indicated that a nominal stoichiometric amount of PDP relative to the pyridine rings was present in the sample. In addition, SAXS measurements indicated indirectly, but conclusively, that PDP remained hydrogen-bonded to the pyridine in electrospun fibers: the SAXS pattern of electrospun PS-*b*-P4VP(PDP)$_{1.0}$ (Fig. 5) shows a distinct peak at scattering vector value, $q = 0.16$ Å^{-1}, roughly corresponding to the long period $L_P = 39$ Å of a lamellar structure of bulk PV4P(PDP)$_{1.0}$ known from our previous work.[12,30] The second-order peak is not resolved here, but it is known to be very small, because of the roughly similar thicknesses of the polar and the non-polar layers. These results indicate that, despite the rough processing conditions during electrospinning, hydrogen-bonding between the amphiphile and the diblock copolymer does not break, i.e., electrospinning does not "purge" the existing supramolecular complexes.

Finally, it has been previously observed in bulk, that if P4VP(PDP)$_{1.0}$ forms self-assembled cylinders within the glassy PS matrix, partially emptied cylinders with P4VP brushes at the pore walls can be obtained upon cleaving PDP.[16] This encouraged us to study porous electrospun fibers using a similar concept, in which case the dark P4VP(PDP) domains of Figures 3b,c should be partially emptied to form pores. Amphiphiles were extracted from the electrospun fibers with methanol. This was confirmed with ^{1}H NMR, as the distinct peaks of PDP were not observed after extraction (peaks were at $\delta = 2.56$ (t, Ar–CH_2–R, PDP) and at $\delta = 0.89$ (t, 3H, CH_3, PDP)). This shows, conclusively, that the amphiphile was extracted successfully from the structure, thus creating pores. As in the corresponding bulk complexes, the glassy PS matrix is expected to prevent the collapse of the pores.[16]

Porous structures in electrospun fibers—whose formation was based on selective degradation (i.e., solvent extraction or thermal degradation) of one component of phase separated polymer blend fibers—have been observed earlier.[31,32] Various reports on surface porosity of electrospun fibers have been published, and several pore-formation mechanisms have been suggested.[9,33,34] Porosity might stem from the phase separation between the polymer and a highly volatile solvent,[9] condensation of humidity on the fibers due to rapid solvent evaporation,[34] or from a combination of the above-mentioned processes.[33] Despite the uncertainties concerning the actual mechanisms, similar pore diameters and shapes have been observed, with sizes ranging typically from 100 to 400 nm. However, in some cases, pores with diameter as small as 20 nm were observed.

In contrast to the other techniques, our method allows combination of pore size control and control of the surface activity at the pore walls because of polymer brushes on their surfaces. In addition, the present self-assembly seems to lead to pore sizes that are typically much smaller than have been observed in previous surface-porosity studies.[9,33,34] It seems evident that self-assembly may ultimately offer feasible tools to obtain structures uniformly positioned throughout the fiber, but requires considerable work to optimize the materials and processes used.

We showed that electrospun mesoscale fibers can be prepared by using amphiphiles hydrogen-bonded to block copolymers that have internal hierarchical self-assembly. The amphiphile can be cleaved from the structure by using selective solvents. With this method, the thickness of the fibers can be tuned by adjusting the spinning conditions and the size of the pores can be controlled by the choice of polymer. Such materials may have applications as filters or in functional fabrics.

Experimental

Materials and Sample Preparation: 3-*n*-pentadecylphenol (PDP) (Aldrich, purity 98 wt.-%) was purified by recrystallizing twice from petrol ether. Polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) was provided by Polymer Source Inc. A concentrated (13 wt.-%) solution of PS-*b*-P4VP(PDP)$_{1.0}$ in *N*,*N*-dimethylformamide (DMF) was prepared using PS-*b*-P4VP (molecular weight 238 100 g mol^{-1} and 49 500 g mol^{-1} for PS and P4VP, respectively; polydispersity: 1.23) by combining the PS-*b*-P4VP/DMF and PDP/DMF solutions. DMF was provided by Riedel de Haën (purity 99 wt.-%). PS-*b*-P4VP (molecular weights: 301 000 g mol^{-1} and 19 600 g mol^{-1} for PS and P4VP, respectively; polydispersity 1.19) was also used to prepare the complexes and, in this case, the concentration of PS-*b*-P4VP(PDP)$_{1.0}$ in DMF was 15.1 wt.-%.

Electrospinning: The apparatus consisted of a syringe, a metal needle (18 gauge) with a positive voltage (+30 kV), and a target plate of the opposite voltage (–30 kV). The syringe was filled with the polymer solution that was fed using a capillary method, without external pressure. The voltage was applied to the solution by attaching the needle to a voltage source (Simco Chargemaster BP 50). A commercial aluminum foil substrate was attached to the receiving plate. An applied field of 3.4 kV cm^{-1} and a deposition distance of 17.5 cm were used. To facilitate TEM, some of the sections were microtomed from fibers spun on a rotating collector (see Fig. 3c, and Figs. 4b,c). The solution was inserted into an 18 gauge needle with a positive voltage of 50 kV (Fig. 3c) or 30 kV (Figs. 4b,c). The rotating collector was grounded. The electrospun fibers were collected onto a polyimide film attached to the edge of the rotating disc collector. The distance between the tip of the needle and the surface of the collector disc was 10.0 cm. The surface speed of the collector was 35 m s^{-1}. Both experiments were carried out under ambient conditions.

Atomic Force Microscopy: AFM was performed using a Digital Instruments Nanoscope III microscope in TappingMode. Height and phase images were recorded simultaneously.

Transmission Electron Microscopy: The bulk sample of the PS-*b*-P4VP(PDP)$_{1.0}$ complex was first annealed for 6 days at 150 °C in a 2 bar (1 bar = 10^5 Pa) nitrogen atmosphere, and then for one day at 120 °C, in order to minimize the unwanted effects of the phase transitions, such as morphology changes and PDP becoming soluble in PS [4,12]. After annealing, the sample was embedded in epoxy and cured overnight at 60 °C. Aligned electrospun fibers were cast in epoxy stepwise: First, a droplet of rhodamine 6G-stained (LC 5900, Lambda Physik), low-viscosity epoxy was inserted, cast, and cured (overnight at 60 °C) on top of the polyimide substrate, in order to highlight the aligned fiber layer. Then, the stained epoxy was cast in standard unstained epoxy and cured overnight at 60 °C. Samples were cut using a Leica Ultracut UCT ultramicrotome and a diamond knife. Thin sections (ca. 70 nm) were microtomed at room temperature and collected on a 600-mesh copper grid. Sections were stained with iodine for 1 h to improve contrast. Bright-field TEM was performed using a Tecnai 12 transmission electron microscope operating at an accelerating voltage of 60 or 120 kV.

^1H *NMR*: Proton NMR spectra were measured on a Bruker Avance-400 spectrometer operating at 400 MHz. The delays used were 25 and 1 s with PDP. Spectra were recorded in deuterated chloroform.

Small-Angle X-Ray Scattering: The electrospun fibers were removed from the substrate foil and collected on a sample holder for SAXS studies. Pure PS-*b*-P4VP block copolymer and PDP were measured in bulk form. A conventional, sealed X-ray tube was used. Cu Kα radiation (wavelength $\lambda = 1.54$ Å) was monochromatized with a totally reflecting mirror (Huber small-angle chamber 701). The incident beam was collimated to a "point-like" using slits. The distance between the sample and the two-dimensional detector (Bruker AXS) was 500 mm, and the scattering vector range was from 0.01 to 0.4 Å^{-1}; the scattering angle was 2. The pixel q values were calibrated using the silver behenate standard. Corrections for spatial distortion and flood field we made using an Fe-55 source and SAXS 4.1.09-program (Bruker AXS, Karlsruhe, Germany).

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Cobalt–Carbon Spheres: Pyrolysis of Dicobalthexacarbonyl-Functionalized Poly(*p*-phenyleneethynylene)s**

By *Stefan Scholz*, *Peter J. Leech*, *Brian C. Englert*, *William Sommer*, *Marcus Weck*, and *Uwe H. F. Bunz**

Micrometer-sized, spherical, non-fullerene carbon is found in meteorites.[1] Similar spheres have been prepared in the laboratory by pyrolysis of a) polyethylene/poly(vinyl chloride) (PVC) mixtures under high pressure, b) methane over an (undisclosed) mixed metal oxide catalyst, c) aqueous acidic solutions of glucose, d) poly(tetrafluoroethylene) (PTFE) in supercritical water, e) ferrocene, f) hexachlorobenzene with sodium metal in an autoclave, and g) tetrachloromethane with sodium amide.[2–7] In cases where transition metals are involved in the process, metal kernels were observed in the center of the spheres as they seem to function either as a catalyst and/or as a nucleation site.[4] Spheres in which the metal is distributed evenly and homogeneously (either as an alloy or as a carbide/ceramic) are unknown:[2–7] the high-yield formation of homogeneous cobalt/carbon spheres by pyrolysis of metallated poly(*p*-phenyleneethynylene) (PPE **7a**) is reported.

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Tetrabenzohexadehydro[20]annulene (**1**) explodes to form carbon nanotubes and onions.[8] Trisdicobalt hexacarbonyl complex **2**, the dicobalthexacarbonyl complex of tolane (**3**), and a multinuclear cobalt complex of a hexaalkynylated hexabenzocoronene derivative (**4**) do likewise, but under just conflagration (as opposed to explosion) or even without visible heat evolution.[9–11] The pyrolytic approach works for the ferrocene-ligated dehydroannulene **5**, which deflagrates into bagel-shaped, tube-like all-carbon objects.[12] Structures **1**–**5** are shown in Figure 1. Synthesis and investigation of the thermal decomposition of metallated PPEs **7** was a natural yet promising extension of these reports.

Post-functionalization of PPEs[13] is difficult but reduction or appendage of organo–platinum fragments[14,15] has been described. The PPEs **6a–c** reacted in good-to-excellent yields (Scheme 1) with dicobalt octacarbonyl in toluene (room temperature) to give the metallated species **7a–c** after precipitation into methanol.[13,16] Both IR and NMR spectroscopy indicate complete occupancy of the alkyne sites by dicobalt hexacarbonyl fragments. The organometallic PPE **7a** is intrinsically less soluble than its precursor **6a**. A sample of **7a** of high solubility was produced when PPE **6a** of low molecular weight ($P_n = 15$, where P_n is the degree of polymerization) was reacted with dicobalt octacarbonyl. The diagnostic signals in the ^{13}C NMR spectrum of **6a** (δ = 93.0, alkyne; 122.7, 132.3, 141.8 arene)[13] changed upon complexation, and signals of **7a** were recorded at δ = 95.9 (complexed alkyne), 132.6, 136.9, 139.4 (arene) and 199.3 (Co–C≡O). The IR spectrum of **7a** differs from that of **6a** (2200 cm^{-1} weak, alkyne stretch; 1722, 1701 cm^{-1}, strong). The alkyne stretch has disappeared and a new set of intense IR bands has appeared for **7a** at 2081, 2050, 2025, and 2004 cm^{-1}, representing the C–O stretch vibrations of the carbonyl ligands. These C–O stretch vibrations are shifted with respect of those of $Co_2(CO)_8$, assuring that no unreacted cobalt octacarbonyl was left in the product.[17] The reaction of **7a** with HCl in chloroform leads to full demetallation and the re-isolation of intact **6a**, as expected for a carbonyl complex. Attempts to make **7a** more lipophilic by a ligand exchange reaction with triphenylphosphine furnished a material with abysmally low solubility; the use of tributylphosphine should lead to a more soluble polymer.

The metallation of **6b** and the alkoxy-PPE **6c** was likewise facile and gave the polycomplexes **7b** and **7c** in excellent yields as greenish-black materials (Scheme 1). Their structures are in accord with the obtained spectroscopic data. The clean reaction of PPEs **6** with dicobalt octacarbonyl is gratifying and in agreement with recent results by Manners and co-workers regarding the complexation of side-chain alkynyl-appended polyferrocenylsilanes by dicobalt octacarbonyl.[16]

Pyrolysis of **7a** with a heat gun (!) or, more controlled, for 1 h in a tube furnace at 650 °C under nitrogen, formed microscopic spheres (Fig. 2a) as sole product. If the pyrolysis of **7a** is conducted at higher temperatures and/or for longer times, occasionally octahedral cobalt nanocrystals are observed. Upon pyrolysis of **7b**, however, misshapen small tubes form (Fig. 2b). An inset shows the stubby tubes at higher magnification. Upon

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